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*Publication date:*  
2013

*Document Version*  
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

*Citation (APA):*  
Arvaniti, O. S., Symсарis, E. C., Andersen, H. R., Hwang, Y., Antoniou, M. G., Nikolaos, T. S., & Athanasios, S. S. (2013). *Removal of perfluorinated compounds from water with Activated Carbon and Advanced Oxidation Processes (AOPs)*. Poster session presented at Micropol & Ecohazard 2013, the 8th IWA Specialist Conference on Assessment and Control of Micropollutants/Hazardous Substances in Water, Zurich, Switzerland.

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# Removal of perfluorinated compounds from water with Activated Carbon and Advanced Oxidation Processes (AOPs).

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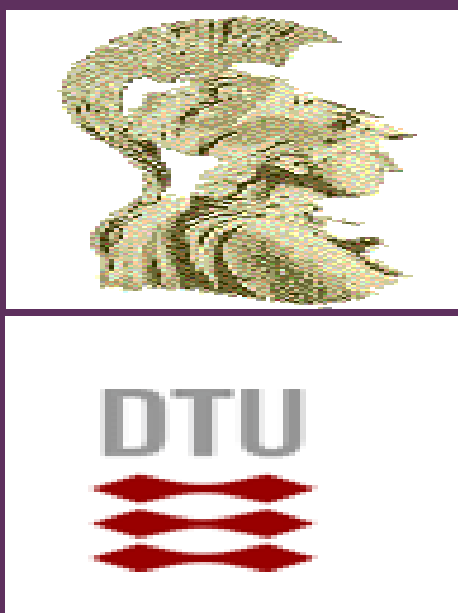
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## INTRODUCTION

Perfluorinated Compounds (PFCs) are persistent micropollutants that have been detected in various environmental and biological matrices worldwide. Monitoring studies in Sewage Treatment Plants (STPs) have shown that these compounds are not significantly removed during conventional wastewater treatment. During the last years, scientific research has been focused on practices that can reduce micropollutants' concentration in wastewater effluents. However, there is limited data about the removal of PFCs using Advanced Oxidation Processes (AOPs) and Activated Carbon (AC). Most of the published data refers to Perfluorooctanoic acid (PFOA) and Perfluorooctane sulfonate (PFOS), while no information is available for the other PFCs.

The aim of this work was to investigate the removal of 6 PFCs (C5, C8 to C11 carboxylic acids and C8 sulfonic acid) in water using a) activated carbon (Powdered Activated Carbon; PAC, Granular Activated Carbon; GAC), b) advanced oxidation processes such as: UV/H<sub>2</sub>O<sub>2</sub>, UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and c) reductive treatments based on nano Zero Valent Iron (nZVI). The percentage removal was calculated for each target compound using the above techniques.

## EXPERIMENTAL SET UP

### Activated carbon experiments.

- Two types of activated carbon (Powdered Activated Carbon; PAC, Granular Activated Carbon; GAC) were used for the removal of PFCs.
- Each type of activated carbon was soaked in pure water for 24 h to remove the impurities
- Then dried in an oven at 105 °C for 48 h.
- Afterwards, AC was crushed by a mortar, screened and stored in a desiccator.
- Initially, the equilibrium time was investigated for each target compound using each type of AC.
- Known amount of AC and target compounds were mixed and samples were taken at predetermined time intervals (0, 4, 8, 12, 18, 24, 48 h).
- Finally, sorption experiments were performed with each type of AC (0.1 g L<sup>-1</sup>) at different pH, [Na<sup>+</sup>], [Ca<sup>2+</sup>] (Table 1). All experiments were conducted in triplicate.

### AOPs experiments.

- Two AOPs (UV/H<sub>2</sub>O<sub>2</sub>, UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) were used for PFVs removal.
- The experiments were performed in a quasi-collimated beam apparatus.
- Low pressure lamps were utilized.
- Initially, pure water was spiked with mixed solution of PFCs (known concentration of 0.2 mg L<sup>-1</sup>).
- The treated solution was 100 mL.
- Afterwards, two doses were investigated for each oxidant (Table 2).
- Samples were taken at predetermined time intervals.
- Blank experiments with no oxidant were also performed to exclude the role of photolysis on PFCs removal.
- Control experiments with no oxidant were also performed to exclude the role of other factors on PFCs removal (e.g. sorption on the flask)

### nanoZVI experiments.

- Three types of nanoZVI (dry nanoZVI, synthetic liquid nanoZVI and synthetic liquid nanoZVI with clay) were used for the removal of PFCs.
- Initially, citric buffer 20 mM was spiked with mixed solution of PFCs.
- The treated solution was 100 mL.
- Afterwards, different concentrations of micronized ZVI (10, 100, 1000 mg L<sup>-1</sup>) were added in each reactor.
- Samples were taken at predetermined treatment time (1, 3, 24 h).
- Control experiments with no nanoZVI were also performed to exclude the role of other factors on PFCs removal (e.g. sorption on the reactor).
- Finally, the influence of solution pH (3, 5, 7) and temperature (20°, 55°) were studied (Table 3). All experiments were conducted in triplicate.

Table 1. Description of sorption experiments (all experiments in triplicate).

Types	PFCs conc. (mg L <sup>-1</sup> )	pH	Na <sup>+</sup> / Ca <sup>2+</sup> (mM)
Powdered / Granular Activated Carbon	0.5	6	-
		7	1
			10
			100
		8	-

Table 2. Experimental design of AOPs experiments.

Types	PFCs conc. (mg L <sup>-1</sup> )	oxidant conc. (mg L <sup>-1</sup> )	Irradiation time (hours)
Control	0.2	-	0
Blank	0.2	-	12
Sample	0.2	10 (S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> )	12
Sample	0.2	100 (S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> )	12
Blank	0.2	-	24
Sample	0.2	20 (H <sub>2</sub> O <sub>2</sub> )	24
Sample	0.2	200 (H <sub>2</sub> O <sub>2</sub> )	24

Table 3. Experimental design of nanoZVI experiments (all experiments in triplicate).

Types	PFCs conc. (mg L <sup>-1</sup> )	nanoZVI conc. (mg L <sup>-1</sup> )	pH	T (°C)
dry nanoZVI, liquid nanoZVI, liquid nanoZVI with clay	0.2	10, 100, 1000	3	20
			3	55
			5	20
			5	55
			7	20
			7	55

## RESULTS AND DISCUSSION

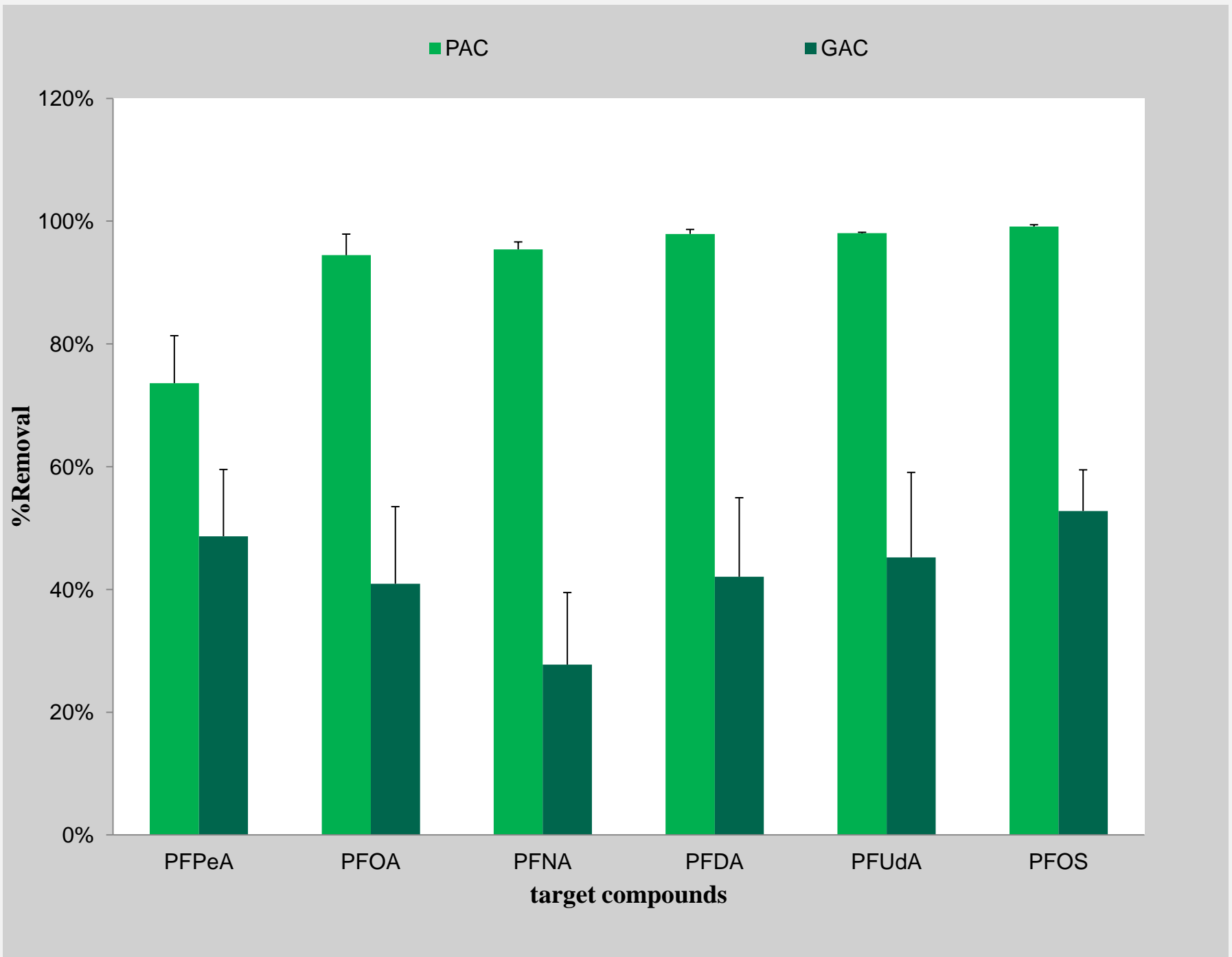


Figure 1. Removal of PFCs using different types of activated carbon (experimental conditions: pH =7)

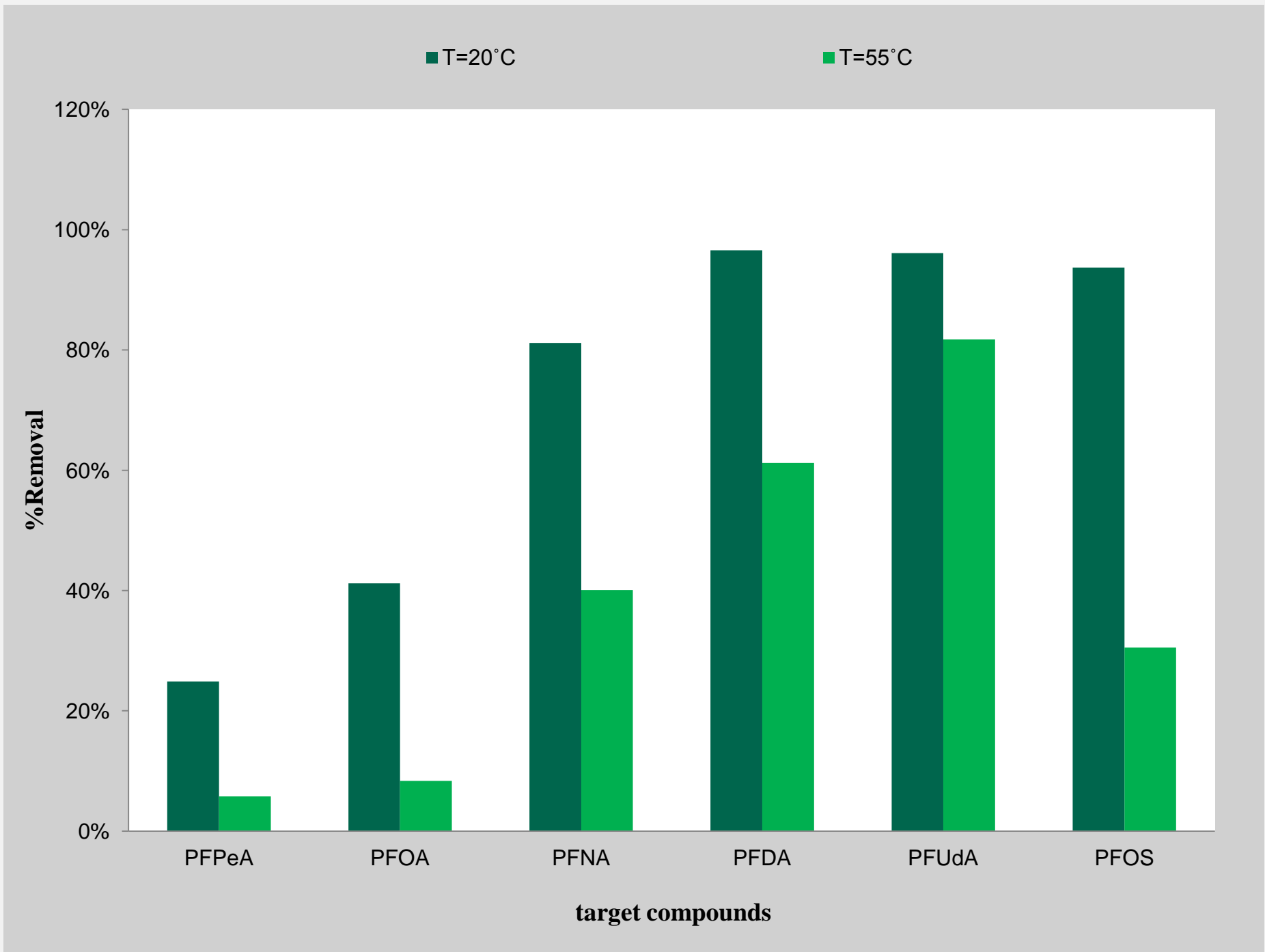


Figure 3. Effect of temperature on the removal of PFCs using liquid nanoZVI with clay (experimental conditions: pH=3, 1000 mg L<sup>-1</sup> nZVI)

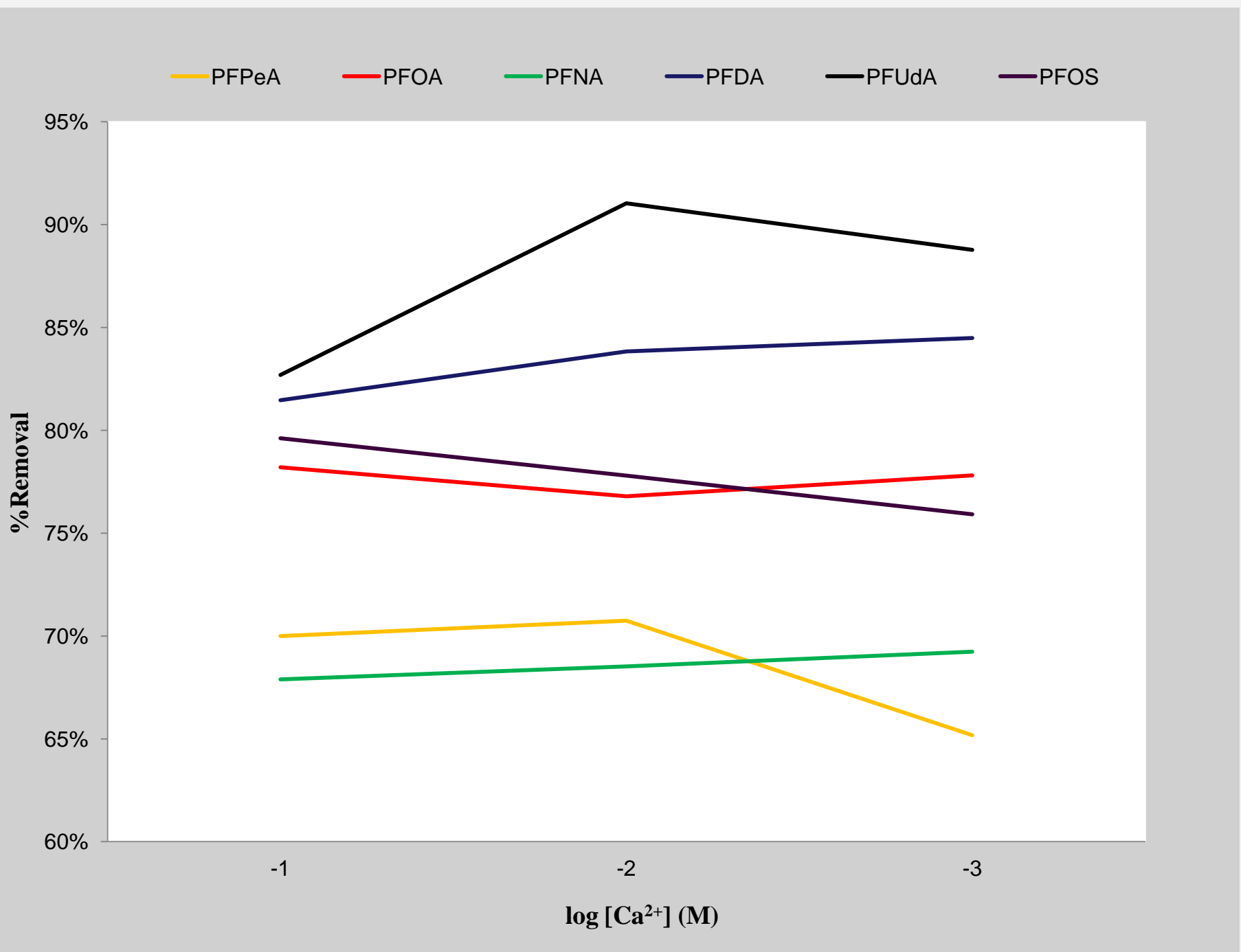


Figure 2. Effect of Ca<sup>2+</sup> on the removal of PFCs using GAC.

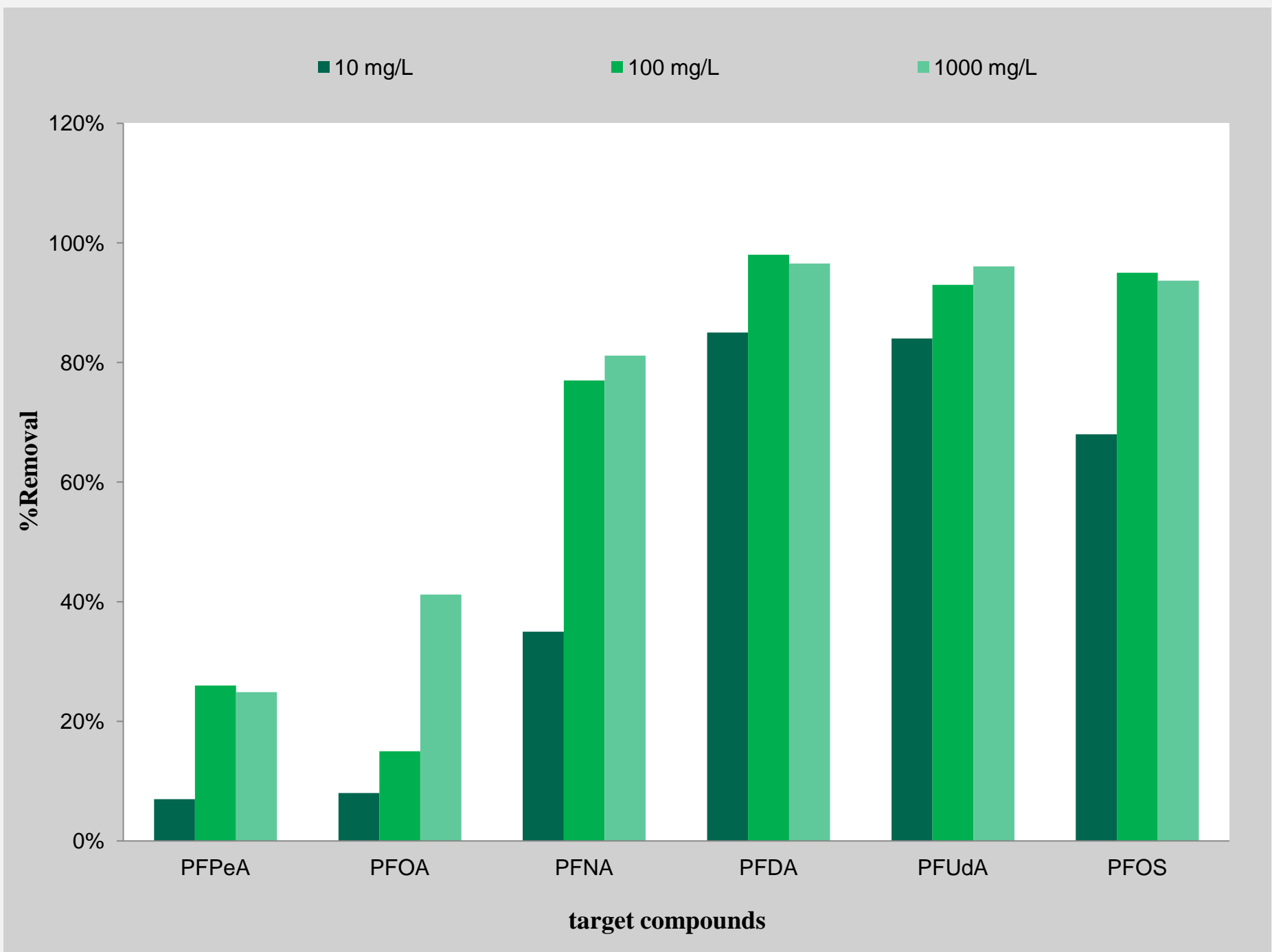


Figure 4. Effect of different concentrations of liquid nanoZVI with clay on removal of PFCs (experimental conditions: pH=3, T=20°C)

### AOPs Experiments

- No significant PFCs removal was observed for the experimental conditions used (data not shown).

### Activated Carbon Experiments

- In AC experiments, the equilibrium time was reached within 4 and 24 hours using PAC and GAC, respectively.
- Among different types of AC, higher removal for all PFCs was observed for PAC (Figure 1).
- Sorption of PFCs on AC was not affected at pH values tested (6-8).
- No significant effect on PFCs sorption was observed when different Ca<sup>2+</sup> and Na<sup>+</sup> concentrations were used for both types of AC. In Figure 2, the results from Ca<sup>2+</sup> /GAC experiments are shown.

### nZVI Experiments

- PFCs were removed in the presence of liquid nanoZVI with clay, while no significant removal was observed using dry and liquid nanoZVI.
- Higher PFCs removal was observed at pH 3 comparing to pH 5 and 7.
- The removal of PFCs increased with decrease of temperature (Figure 3).
- Higher removal was observed with increase of C - F chain for perfluorinated carboxylic acids, PFCAs (Figure 3).
- Higher removal was observed with increase of concentration of nanoZVI from 10 to 100 mg L<sup>-1</sup>, no significant increase was observed from 100 to 1000 mg L<sup>-1</sup> (excepting PFOA) (Figure 4).

## ACKNOWLEDGEMENTS

This project was implemented under the Operational Program «Education and Lifelong Learning» and funded by the European Union (European Social Fund) and National Resources – HRAKLEITOS II

